TRACE-P C_1 - C_5 Alkyl Nitrates: Production, Evolution and Distribution

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Planned TRACE-P alkyl nitrate papers:

- **1. Distribution:** "Latitudinal and vertical distributions of C₁-C₅ alkyl nitrates in the troposphere over the western Pacific Ocean during TRACE-P"
- 2. Production and evolution (kinetics): "Production and evolution of C₂-C₅ alkyl nitrates in tropospheric air influenced by Asian outflow"



Alkyl Nitrate Measurements during TRACE-P

Parent RH Daughter RONO₂

C₁ methane methyl nitrate (MeONO₂)

C₂ ethane ethyl nitrate (EtONO₂)

C₃ propane 1-propyl nitrate (1-PrONO₂)

2-propyl nitrate (2-PrONO₂)

 $\mathbf{C_4}$ *n*-butane 2-butyl nitrate (2-BuONO₂)

C₅ *n*-pentane 2-pentyl nitrate (2-PeONO₂) 3-pentyl nitrate (3-PeONO₂)

Detection: 0.02 pptv

Precision: 2%

Accuracy: 10-20%

Alkyl Nitrates

- low reactivity: serve as reservoir for longrange transport of NO_x
- explain lack of closure in NO_y budget
 - Continents: RONO₂ <10% NO_y
 [e.g. Ridley et al., 1990; Flocke et al., 1991]
 - MBL PTA: RONO₂ 20-80% NO_y
 [Talbot et al., 2000]
- estimate photochemical age using [RONO₂] / [parent RH]
- unique opportunity to compare field measurements with newly published values from laboratory studies



Alkyl Nitrate Production

Two pathways:

1. Marine emissions

- importance ↓ for ↑ carbon number
- varies with latitude

2. Photochemical production

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(1) \mathbf{RH} + \mathbf{OH} \rightarrow \mathbf{R} + \mathbf{H}_2\mathbf{O} k_1, \alpha_1

(2) \mathbf{R} \cdot + \mathbf{O}_2 \rightarrow \mathbf{RO}_2 \cdot k_2

(3a) \mathbf{RO}_2 \cdot + \mathbf{NO} \rightarrow \mathbf{RONO}_2 k_{3a}, \alpha_2

(3b) \mathbf{RO}_2 \cdot + \mathbf{NO} \rightarrow \mathbf{RO} + \mathbf{NO}_2 k_{3b}, 1-\alpha_2
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k = reaction rate constant α = branching ratio